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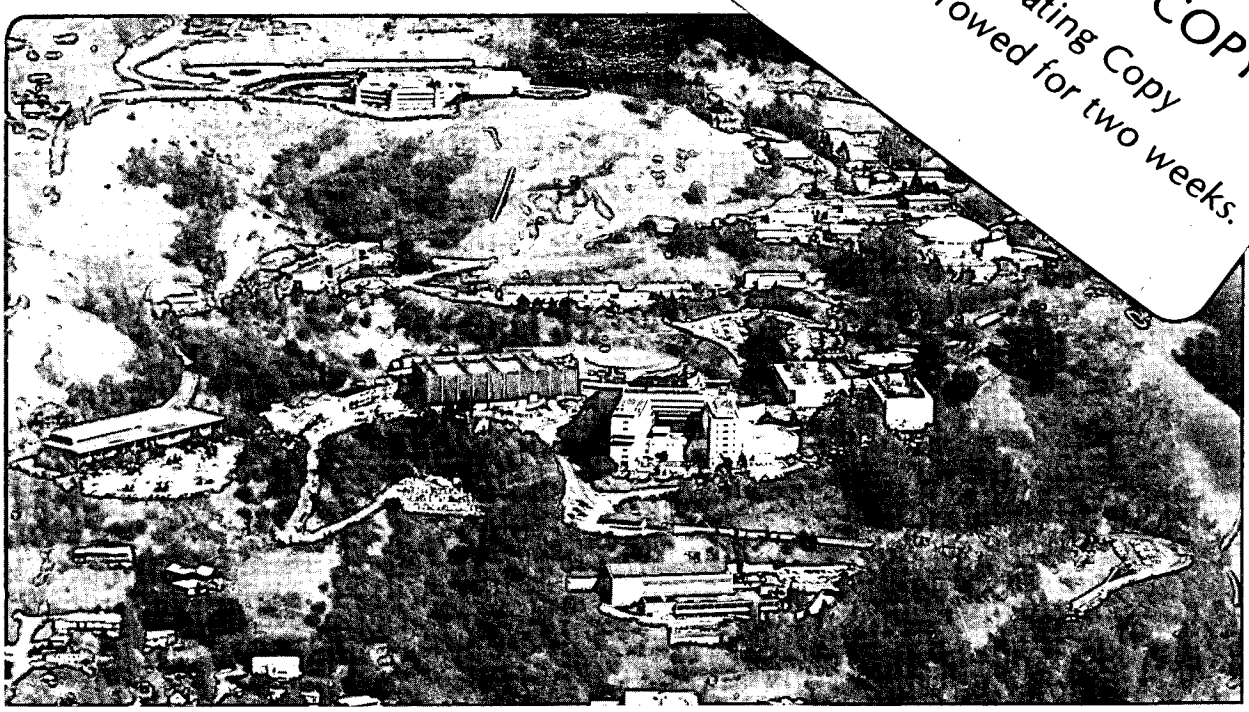

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DISCLAIMER

Infrared Absorption Study of Neutron-Transmutation-Doped Germanium

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Using high-resolution far-infrared Fourier transform absorption spectroscopy and Hall effect measurements we have studied the evolution of the shallow acceptor and donor impurity levels in germanium during and after the neutron transmutation doping (NTD) process. Our results show unambiguously that the gallium acceptor level concentration equals the concentration of transmutated ^{70}Ge atoms during the whole process indicating that neither recoil during transmutation nor gallium-defect complex formation play significant roles. The arsenic donor levels appear at full concentration only after annealing for one hour at 450°C. We show that this is due to donor-radiation defect complex formation. Again recoil does not play a significant role.

I. INTRODUCTION

Neutron transmutation doping (NTD) is a well established technique for achieving uniform doping of bulk semiconductors. The technique makes use of thermal neutrons penetrating a semiconductor. The various isotopes in the semiconductor capture neutrons and decay into other host atoms or dopants. Due to the uniformity of the flux of thermal neutrons and the uniform distribution of isotopes in the semiconductor material, NTD results in extremely homogeneous doping. For high voltage, high power silicon devices, uniform doping is crucial and NTD has evolved as the doping technique of choice[1]. The NTD technique has been applied to germanium, gallium arsenide and other semiconductors.

NTD germanium has been extensively used in the study of impurity hopping conduction[2] and in the development of cryogenic bolometers[3,4]. The main interest in such material stems from its extreme doping homogeneity and reproducibility. Whereas thermal neutrons transmutate germanium nuclei into dopant atoms, fast neutrons which unavoidably are part of the NTD process produce radiation damage.

When thermal neutrons penetrate germanium, three out of the five stable isotopes participate in the doping process as follows:

$$^{70}Ge(n,\gamma)^{71}Ge \rightarrow {}^{71}Ga(e^- \text{ capture, } t_{1/2} = 11.2 \text{ days})$$

$$^{74}Ge(n,\gamma)^{75}Ge \rightarrow {}^{75}As(\beta^- \text{ decay, } t_{1/2} = 82.2 \text{ min})$$

$$^{76}Ge(n,\gamma)^{77}Ge \rightarrow {}^{77}As(\beta^- \text{ decay, } t_{1/2} = 11.3 \text{ hr})$$

$$\rightarrow {}^{77}Se(\beta^- \text{ decay, } t_{1/2} = 38.8 \text{ hr})$$

The ratio of the concentrations of the different dopants is fixed by the thermal neutron capture cross section and natural abundance of the dopant-producing isotopes.

The doping and defect formation processes are occurring simultaneously in NTD germanium. This leads to many possible interactions between the three different dopants and radiation defects. Numerous studies on the formation and the removal of radiation defects produced by fast neutrons in semiconductors have been reported[5]. Most of these studies have not dealt with NTD germanium. The few previous reports dealing with NTD germanium[6,7] are limited to the recovery of the radiation damage through annealing at different temperatures by measuring the changes in the electrical properties. To study the behavior of each impurity and defect species separately we need to approach this problem with some other techniques. Using infrared absorption spectroscopy, we can identify all the electrically active majority impurities separately. With band-edge light illumination we can simultaneously study minority impurities[8]. Variable temperature Hall effect measurements allow the quantitative determination of the concentration of dopant impurities and radiation defects.

We have focused in this study on the shallow dopant impurities generated by the NTD process and deliberately ignored the investigation of the deep levels which is a considerably more complex issue because one is dealing with fast neutron damage. The fast neutron energy spectrum and flux can vary significantly from one reactor to another and also within the same reactor. A new study using advanced techniques such as capacitance or current transient spectroscopies and a well characterized neutron spectrum may generate new data which could improve the understanding of neutron damage.

II. EXPERIMENTAL

Slices were cut from an ultra-pure germanium single crystal grown under a nitrogen atmosphere. Hydrogen-atmosphere-grown crystals were deliberately not considered for this experiment because it is known that a very large number of hydrogen-related complexes form in such crystals[9,10]. The concentrations of all residual electrically active impurities were less than $10^{11}cm^{-3}$ and the thickness of the slices was 2 mm. The polish etched and cleaned wafers were irradiated with 2×10^{15} thermal neutrons/cm^2 at room temperature in the research reactor at the University of California at Berkeley. The ratio of thermal to fast neutrons was 4. This fluence of thermal neutrons leads to $6 \times 10^{13}cm^{-3}$ gallium and $2 \times 10^{13}cm^{-3}$ arsenic impurities[11]. The selenium concentration produced by this process is about 1×10^{12} cm^{-3} which is very small compared to those of gallium or arsenic and we neglect the contribution of selenium in this study. After neutron irradiation, the samples were annealed at a number of different temperatures for one hour under a flowing argon gas.

Square Hall effect samples (7 x 7) mm^2 were cut from the irradiated slices. Hall effect measurements in the van der Pauw geometry[12] were performed to obtain the carrier concentration and carrier mobility. We used a magnetic field of 3 kG for variable temperature Hall effect measurements and 106 G for 77 K measurements with corrections for the Hall scattering factor for varying conditions[13,14]. Ohmic contacts were made by alloying a small amount of indium on four corners of the sample by heating with a soldering gun for a very short period of time. The sample temperature reached approximately 160°C and the time required to form each contact was about ten seconds. The contacting process induces limited annealing effects in the sample which are negligible compared to the annealing temperatures used. The sample denoted as

"unannealed" is actually annealed 40 sec at 160°C to serve as an accurate reference.

Infrared absorption measurements were done at liquid helium temperature using a far-infrared Michelson interferometer with an instrumental resolution of 1/8 cm^{-1} (= 15.5 μeV). The sample thickness was about 1 mm. To obtain both majority and minority spectra simultaneously, we used band-edge light. The electrons and holes generated by photons with energy above bandgap are captured by the ionized donors and acceptors respectively, yielding them neutral and accessible to absorption spectroscopy. The high energy part of the IR-source, a mercury arc lamp, was used as the band-edge light. The detector used to record the IR signal transmitted through the germanium samples was a stressed gallium-doped germanium photoconductor[15] with a response range from 50 to 200 cm^{-1}. The concentration of impurities was determined by comparing the linear absorption coefficients of a number of ground-to-bound excited state transitions of the NTD samples with well characterized, low compensation, melt-doped samples[16].

III. RESULTS AND DISCUSSION

In Fig. 1a the absorption spectrum of the sample which was thermal neutron doped and fully annealed at 500°C for one hour is shown in the wavenumber range from 62.5 to 125 cm^{-1}. As expected, two hydrogenic series of absorption peaks from gallium acceptor and arsenic donor impurities are clearly visible. The concentrations of each impurity are within 50% of the value expected from the neutron fluence. The main cause of error is expected to come from the inaccuracy of the neutron fluence. The spectrum of the same sample before annealing is shown in Fig. 1b. In this spectrum, only absorption peaks from gallium acceptors are observed while those of the

arsenic donors are absent. The intensities of the absorption peaks of gallium are equal to within 10% in both spectra which means that essentially all gallium impurities are electrically active shallow acceptors with or without annealing. From this experimental observation we deduce two findings: first, the transmutating ^{71}Ge nuclei forming gallium do not recoil from their substitutional positions when capturing a neutron; and second, radiation defects do not bind to the gallium acceptors. Further quantitative proof is derived and shown in Fig. 2. The intensities of the D and C lines of the unannealed sample as a function of time after neutron irradiation increase at the same rate as gallium is formed through the ^{71}Ge electron capture reaction.

From the above information alone, we cannot arrive at definite conclusions about the absence of the arsenic acceptor peaks in Fig. 1b. There are two possibilities for this absence. One is that arsenic impurities do not occupy substitutional positions after the ^{75}Ge β^--decay, and the other is that arsenic atoms do occupy substitutional positions but form complexes with radiation defects. Careful analysis of the recoil conditions and displacement energies shows that there is practically no difference between gallium and arsenic impurities[11,17]. Excluding recoil and displacement we must assume that arsenic donors capture radiation defects (vacancies, etc.) forming complexes. It is well known that vacancies in germanium are mobile at temperatures as low as 65 K[18]. Therefore, it is believed that the vacancies produced by irradiation diffuse to the donor sites and form complexes. The formation of complexes between Group V donor and radiation defects in silicon and germanium has been suggested by many studies[19-21]. Mashovets, et al. also argued, based on vast experimental evidence, that divacancy-donor complexes form in γ-irradiated germanium[22]. In their paper, they showed

that Group V impurities readily combine with divacancies or two separate vacancies and become deep acceptors with energy levels at about 0.1 eV above the top of the valence band. These complexes can be dissociated by annealing above about 80°C, with the temperature of annealing depending slightly on the specific Group V impurity species. To confirm if this model, obtained for γ irradiation, may be applicable for fast neutron damage, we prepared n-type germanium samples and irradiated with the same amount of neutrons as the NTD samples. The concentration of phosphorus before neutron irradiation was 6 x 10^{13} cm^{-3} measured by 77 K Hall effect measurement. Figure 3a is the absorption spectrum of the sample before neutron irradiation. The absorption peaks of phosphorus are clearly shown. Figure 3b is the absorption spectrum taken of the same sample after neutron irradiation. The absorption peaks of gallium acceptors are clearly visible but those of both phosphorus and arsenic are not present. The absorption peaks of the phosphorus and arsenic donors reappear only after annealing at 400°C for one hour and reach their maximum intensity after annealing at 450°C for one hour (Fig. 4). This result supports in part the assumption by Mashovets, et al. at least in the sense that Group V impurities do form complexes with radiation defects thereby losing their donor property. The temperatures at which dissociation of the donor/defect complex occurs, however, are different for neutron and γ irradiation. Early annealing study on oxygen-defect complexes in irradiated germanium showed that there is a general shift to higher annealing temperatures for the neutron-irradiated samples[23]. After neutron irradiation, the absorption peaks from either arsenic or phosphorus did not appear after annealing at 350°C while the dissociation was almost complete at about 100°C in the γ damage study. The concentration resolution limit in our study is about 10^{12} cm^{-3} which means that there was almost no, if any,

dissociation of the defect/donor complexes occurring below an annealing temperature of 350°C. From our results we conclude that these centers are not divacancy/donor complexes but significantly larger defect/donor clusters.

Figure 5 shows the net carrier concentration and mobility of the samples annealed at different temperatures as measured by 77 K Hall effect. The free hole concentration of an unannealed sample is more than ten times that of a fully annealed (500°C) sample. This high concentration of holes in the unannealed sample must be originating from radiation defects other than divacancy/donor complexes because the concentration of donor/defect complexes would be, at most, the same as the concentration of arsenic impurities (2×10^{13} cm^{-3}) which is much lower than the carrier concentration measured in the unannealed sample. The measured carrier concentration decreases as the annealing temperature increases and at 500°C the free hole concentration saturates at the expected value. To find out more about these defect-related acceptors in the unannealed sample, we conducted variable temperature Hall effect measurements. A plot of carrier concentration vs. inverse temperature for the fully annealed and unannealed sample is shown in Fig. 6. The curve for the fully annealed sample shows the saturation region corresponding to a gallium acceptor concentration of 2.5×10^{13} cm^{-3}. The acceptor freeze-out region starts at about 20 K. The characteristic half-slope freeze-out region is not visible because of the high degree of compensation by arsenic donors. The full-slope freeze-out of gallium acceptor yields a gallium acceptor ionization energy of 11 meV in excellent agreement with published values[24]. In the unannealed sample there are additional acceptor levels with a total concentration of 4.5×10^{14} cm^{-3}. The smooth, continuous decrease of the free hole concentration between 300 K and approximately 15 K--the temperature where the curves a and b merge--indicates

that a number of different deep levels with closely spaced energies or a deep level energy continuum must be present. Below about 15 K, the curve for the unannealed sample shows the full-slope freeze-out of the gallium acceptors. The mobility data in Fig. 5 are consistent with the carrier concentration results. The free carrier mobility value of the unannealed sample is lower than that of the annealed sample because of hole scattering caused by the radiation defects. Annealing the sample at increasingly higher temperatures leads to higher hole mobility until it saturates at an annealing temperature of around 500°C. Our results on annealing effects of the electrical properties of NTD germanium agree well with previously published reports[6].

IV. CONCLUSIONS

We have shown with far-infrared absorption spectroscopy and variable temperature Hall effect measurements that gallium impurities produced by neutron transmutation of germanium are electrically active acceptors requiring no annealing. NTD arsenic impurities on the other hand are not electrically active after the NTD process and are believed to form complexes with defects, most likely vacancies, produced by fast neutrons. During annealing at temperatures of at least 400°C, these complexes dissociate and produce arsenic donors. The dominant radiation defects produced by fast neutrons are predominantly acceptors with energy levels spread over a broad range above E_V + 10 meV.

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FIGURE CAPTIONS

Fig. 1. Absorption spectra of NTD samples: a) annealed at 500°C for one hour; b) unannealed.

Fig. 2. Plot of the linear absorption coefficient of D and C absorption lines of gallium acceptor of the unannealed sample vs. time after neutron irradiation.

Fig. 3. a) Absorption spectrum of phosphorus-doped germanium sample (N_p = 6×10^{13} cm^{-3}); b) absorption spectrum of the same sample after neutron irradiation. (Absorption peaks from residual shallow acceptors are also shown in both spectra.)

Fig. 4. Absorption spectrum of phosphorus-doped, NTD germanium sample after annealing at 450°C for one hour.

Fig. 5. Plot of the net-carrier concentration and carrier mobility of NTD germanium sample vs. annealing temperature (measured by 77 K Hall effect).

Fig. 6. Result of variable temperature Hall effect measurement of fully annealed (a) and unannealed (b) NTD germanium sample.

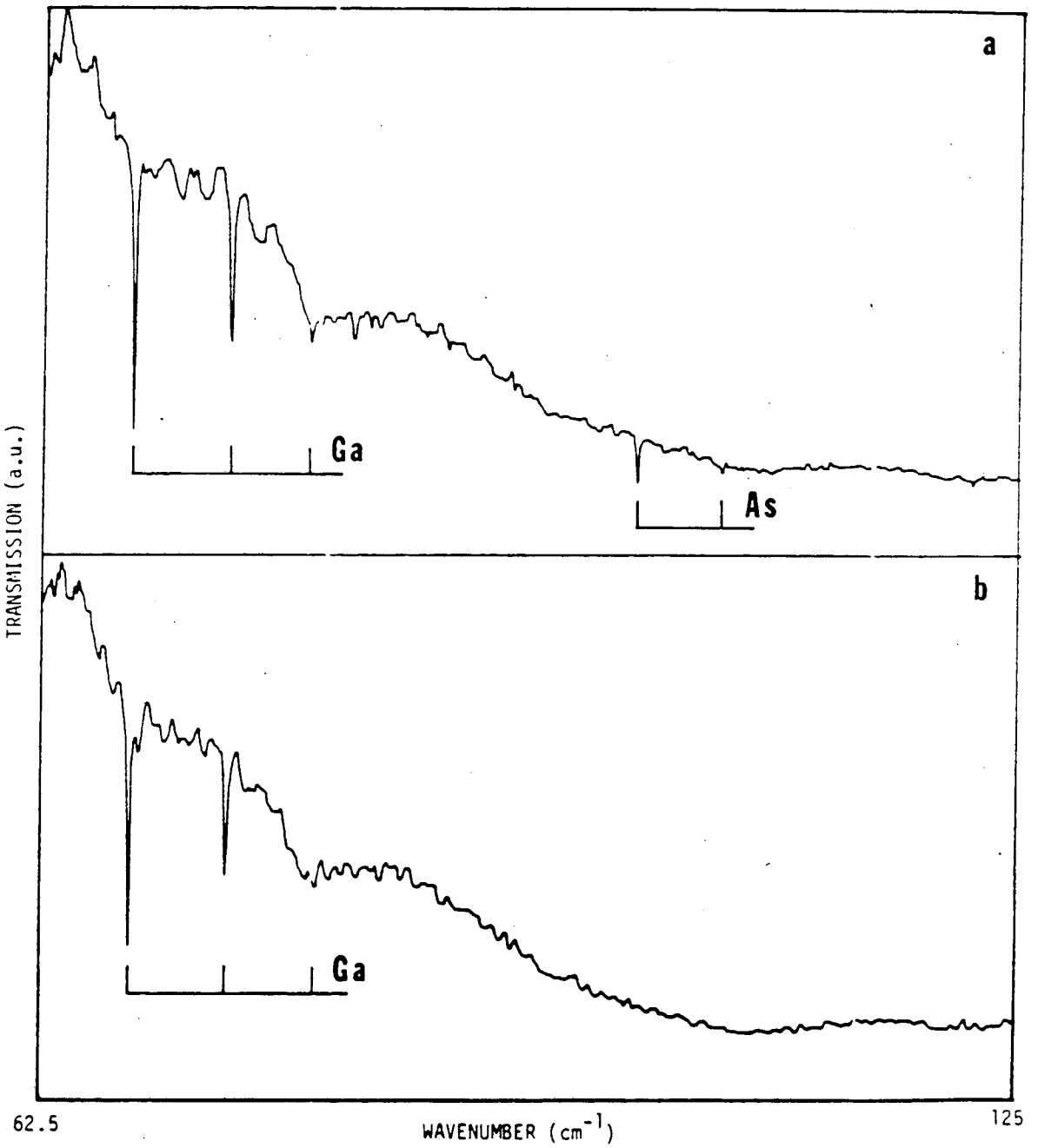
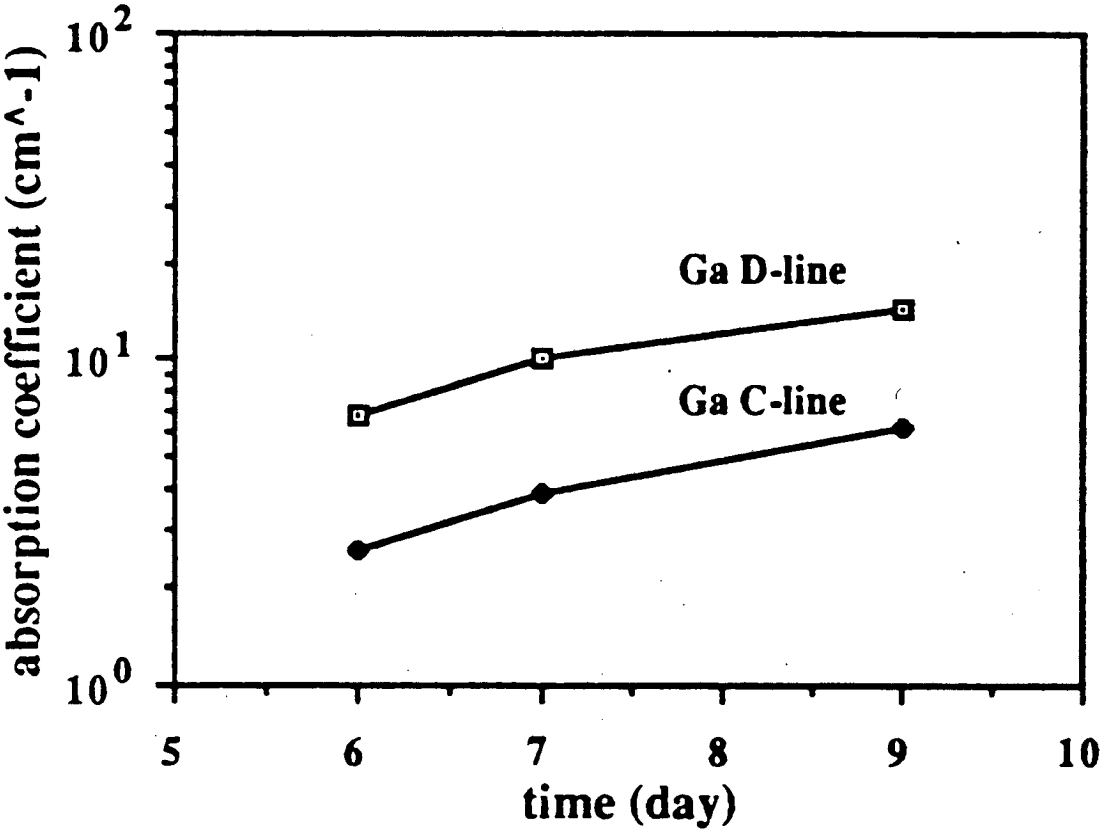

a
Ga
As
b
Ga
TRANSMISSION (a.u.)
62.5
WAVENUMBER (cm^{-1})
125
XBL 882-406

Fig. 1.



XBL 882-410

Fig. 2.

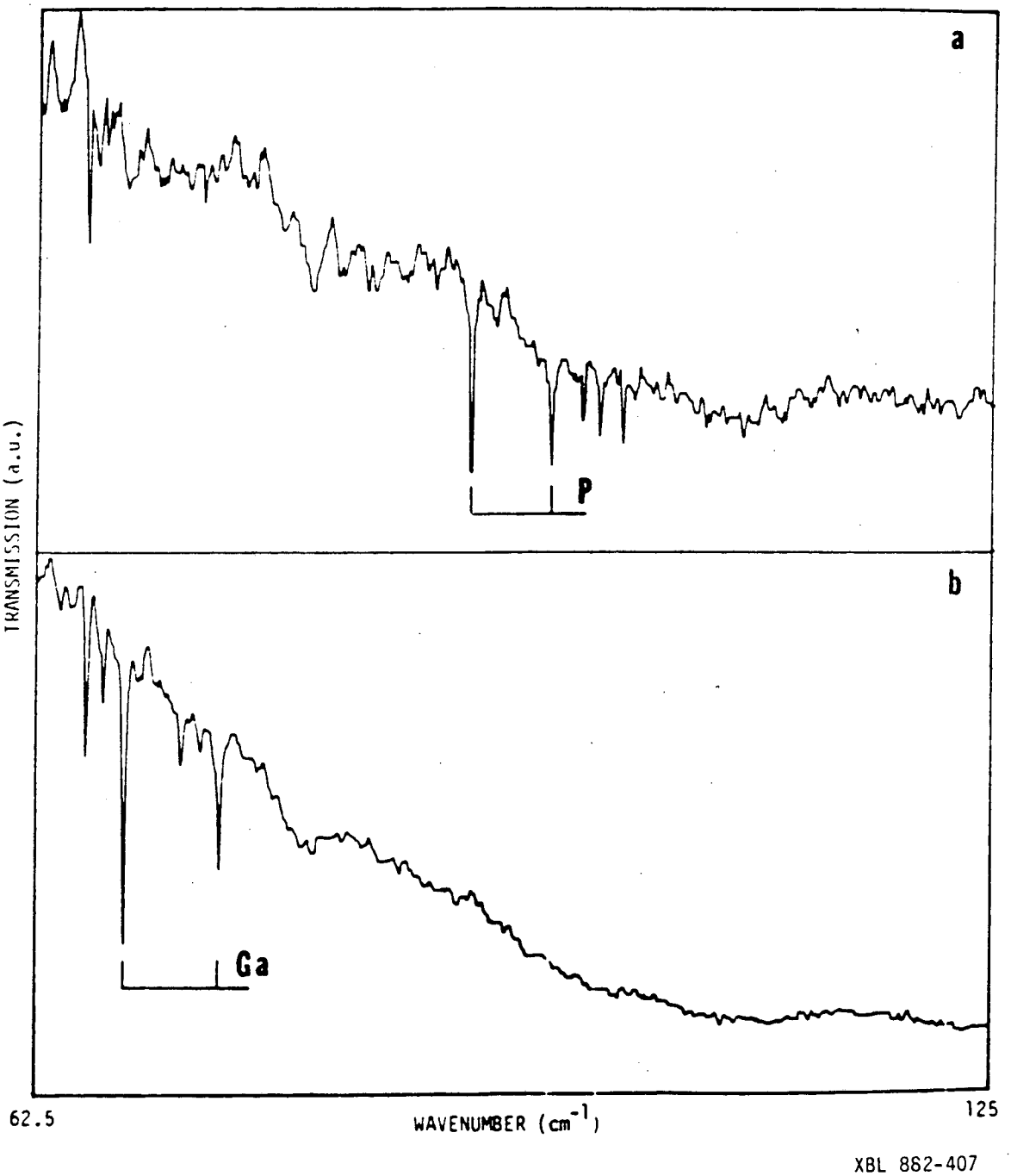
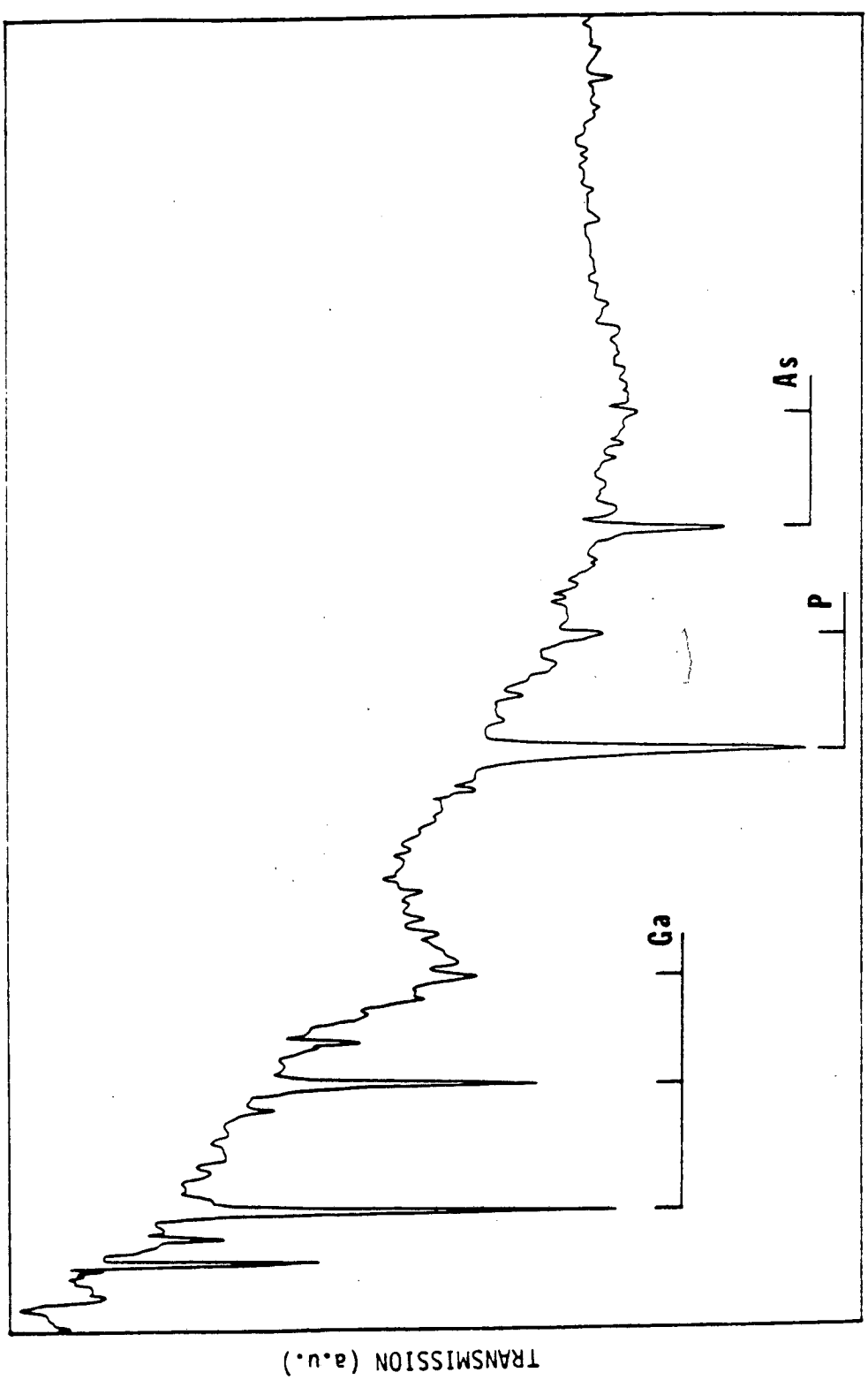
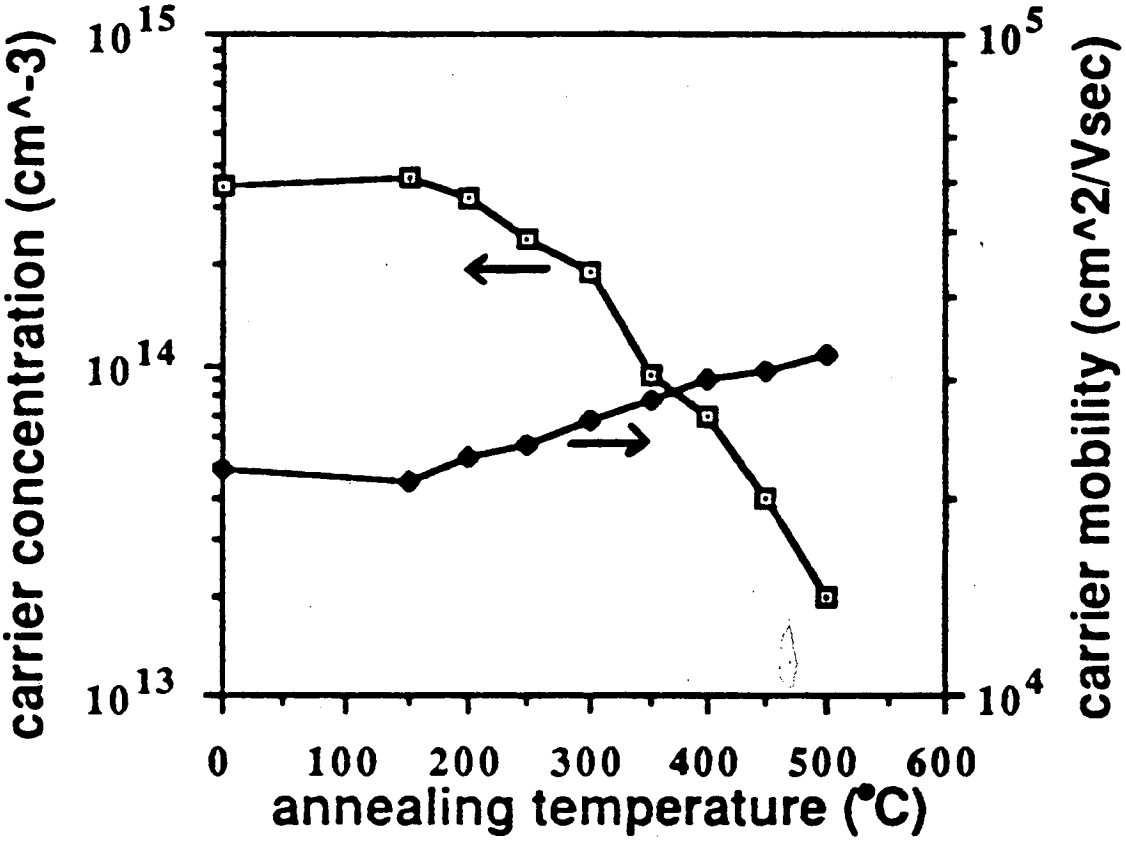


Fig. 3.



XBL 882-408

Fig. 4.



XBL 882-409

Fig. 5.

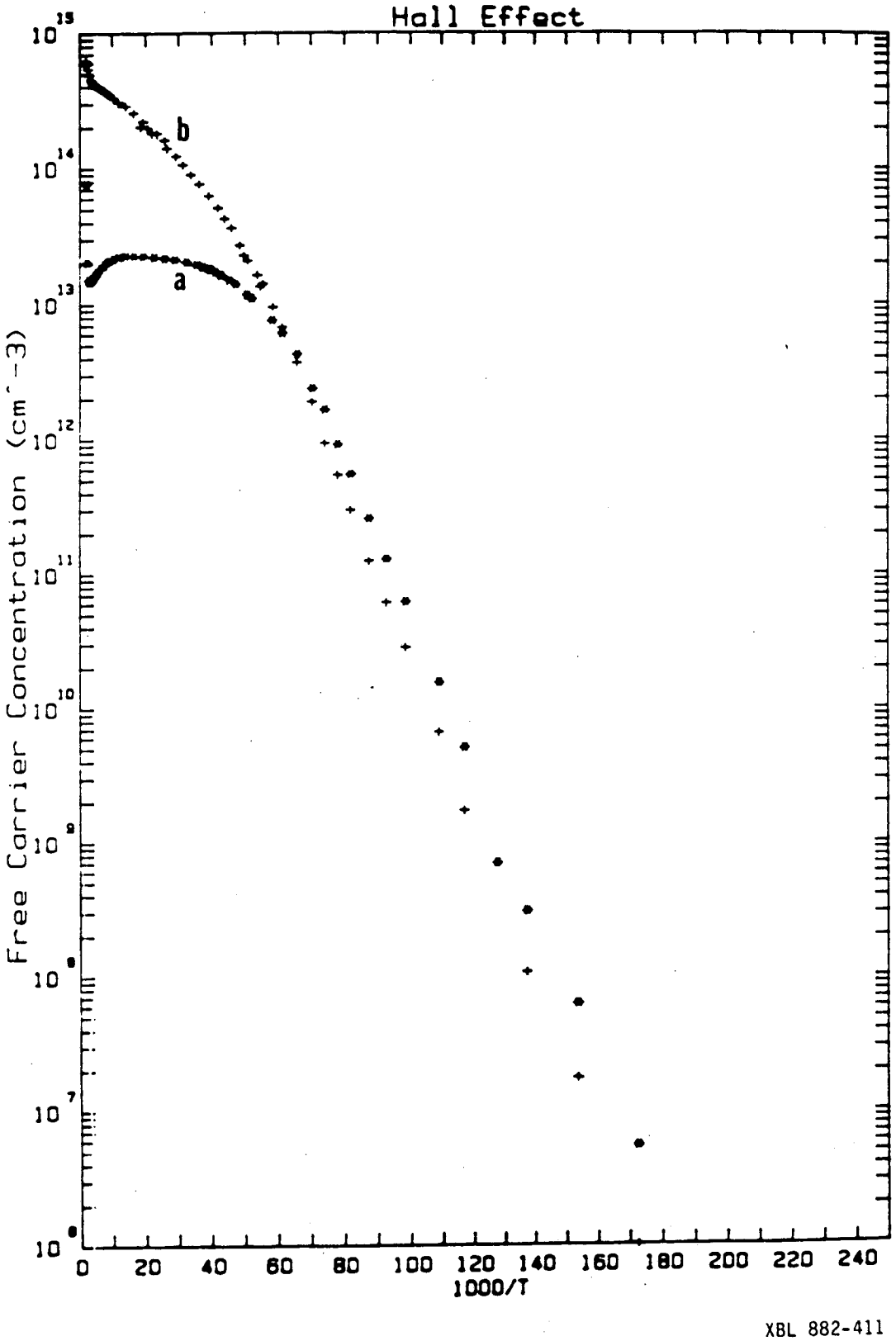

Hall Effect
Free Carrier Concentration (cm^-3)
1000/T
a
b
XBL 882-411

Fig. 6.

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